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Optical constants of beryllium from photoabsorption measurements for x-ray optics applications

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ABSTRACT

Beryllium (Be) has been recently receiving considerable attention as the key material for a range of potential applications in the extreme ultraviolet (EUV) and x-ray region. Most notably, it has been successfully implemented as the spacer material in beryllium-based multilayer mirrors for EUV lithography, achieving experimental reflectivities of about 70% at wavelengths around 11.4 nm. Knowledge of the absorptive and dispersive properties of this material thus becomes important for the modeling of these optics. Experimental photoabsorption results in the region 40-250 eV, derived from transmission measurements on free-standing beryllium foils, are presented in this work. The measured absorption in the region extending a few tens eV below the K edge (111.7 eV) appears to be significantly (up to 50%) lower than the tabulated values. Fine structure above the K edge is also demonstrated in the measurements. These data are incorporated in an updated set for the atomic scattering factors of beryllium, obtained in the range 0.1-30,000 eV. Finally, the Bragg reflectivity of Mo/Be multilayer optics is modeled using the new experimental results.

Keywords: Beryllium, extreme ultraviolet, optical constants, refractive index, x-rays

1. INTRODUCTION

Beryllium is a very important material for a wide variety of commercial and scientific applications, due to its unique properties. It has the lowest stiffness per weight ratio among all metals, very low specific gravity, electrical resistivity and specific heat at cryogenic temperatures. Furthermore, it has very high thermal conductivity, melting point, sound velocity, modulus of elasticity and specific heat at normal and elevated temperatures. Therefore, beryllium found use in many consumer products as a metal, in alloys and salts, and in beryllium oxide ceramics.

Beryllium is relatively transparent to x-rays and has been commonly used as a window at synchrotron beamlines, x-ray detectors and as a bandpass filter for EUV astronomy instruments. In recent years, it has been possible to fabricate multilayer mirrors with beryllium as the spacer material[1,2] operating below the beryllium K edge (111.7 eV or 11.10 nm). High reflectance beryllium-based multilayer coatings designed to operate at 11.4 nm are very attractive for the EUV lithography effort, since the currently considered xenon laser plasma source yields at 11.4 nm a power output up to 4 times higher than at 13.4 nm (the wavelength of operation of Mo/Si, another candidate material pair for EUV multilayer optics). Due to its low atomic number and mass absorption coefficient, beryllium has been suggested as an ideal medium for x-ray refractive lenses, intended for microdiffraction, microfluorescence and coherent imaging experiments; first successful fabrication of such lenses has been recently reported.[3] Other novel applications include the use of mosaic beryllium crystals as quarter-wave plates for magnetic x-ray circular dichroism studies.[4]

Given the aforementioned wealth of applications of beryllium, it is surprising that its optical constants (the real and imaginary part of the refractive index) in certain energy regions are still poorly known. Knowledge of these properties is essential in the modeling of the performance of x-ray optics and in the interpretation of raw x-ray

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data when beryllium is used as a detector window. In this paper we are especially interested in the absorptive and dispersive properties of this material in the EUV/x-ray range, with particular emphasis in the region around the K edge. Recent experimental results for the imaginary part (absorption) of the refractive index are presented and are implemented in dispersion calculations. The present results are discussed in comparison with data previously published in the literature, and with an advanced theoretical model predicting the absorptive behavior in the energy region above the K edge.

2. OPTICAL CONSTANTS FROM PHOTOABSORPTION DATA

The dispersive and absorptive properties of a medium in the EUV and soft x-ray energy range are commonly expressed in terms of the optical constants δ, β of the complex refractive index $n = 1 - \delta + i\beta$. n is in general related to the forward atomic scattering factor $f = f_1 - if_2$ by

$$n^2(E) = 1 - \frac{r_0 n_a}{\pi} \left(\frac{hc}{E}\right)^2 f(E), \tag{1}$$

where $E = h\nu$ is the photon energy, r_0 represents the classical electron radius, n_a (atoms/cm^3) is the atomic density of the material (related to the mass density ρ (g/cm^3) by $n_a = \rho N/M$, N being Avogadro's number and M being the molecular weight of the material), h is Planck's constant and c is the velocity of light. To a good approximation, assuming that $\delta, \beta \ll 1$ in this energy range, eq. (1) becomes

$$n(E) \simeq 1 - \frac{r_0 n_a}{2\pi} \left(\frac{hc}{E}\right)^2 f(E). \tag{2}$$

Thus, in the regime where eq. (2) is valid, one may interchange between the atomic scattering factors f_1, f_2 and the optical constants δ, β, by means of the simple linear expression δ (or β) $= (r_0 n_a/2\pi)\,(hc/E)^2\, f_1$ (or f_2). It is always desirable to obtain experimentally both the real (f_1) and the imaginary (f_2) parts of the atomic scattering factor of a material; this can be achieved with methods such as reflectivity, photoelectric yield, ellipsometry and interferometry. However, these techniques are extremely sensitive to sample contamination in the EUV/x-ray range, therefore their implementation can be often challenging. On the other hand, whenever it is possible to fabricate thin, free-standing film samples of the material under study, absolute photoabsorption data may be used to determine f_2 and dispersion analysis may be applied to calculate f_1. For instance, the absorption coefficient μ (cm^2/g) may be obtained from transmission measurements. Then, f_2 may be determined directly from the experimental results by

$$f_2 = \frac{M}{2r_0 hcN}\, E\, \mu(E) \tag{3}$$

and the Kramers-Kronig relations may be used for the dispersive part f_1,

$$f_1(E) - Z^* = (\pi r_0 hc)^{-1} \int_0^\infty \frac{\epsilon^2\, \mu(\epsilon)}{E^2 - \epsilon^2} d\epsilon, \tag{4}$$

where Z^* represents the atomic number of the material reduced by the relativistic correction $(Z/82.5)^{2.37}$ (see Ref. 5). Transmission versus photon energy measurements are simple and fast to execute, and, as it is going to be explained in Sec. 3, they allow to account for the presence of contamination on the samples and to eliminate its effect on the results. One of the pitfalls of eq. (4) is that it requires accurate information on the absorption throughout the entire spectrum, for the calculation of f_1 at a single photon energy. Obviously, a compilation of results from various energy regions is needed in order to gather the necessary set of photoabsorption data. This task has been performed in the 1993 atomic tables[5] for all materials from Z=1 to Z=92: published data from various experimenters are used in combination with theoretical calculations in order to determine f_2 in the range from 10 to 30,000 eV, and f_1 is calculated via eq. (4).

In Ref. 5, the values of f_2 for beryllium (Z=4) in the energy range below the K edge (111.7 eV) have been obtained exclusively from theoretical calculations, while some experimental data points for the absorption have been used for energies above the edge. In this paper, new results for the absorption of beryllium from transmission measurements in the range 40-250 eV are presented. The new data are compared to those in Ref. 5, and are used in combination with previously published results for energies outside 40-250 eV. An updated set of values for the atomic scattering factors f_1, f_2, is thus obtained in a wide energy range.

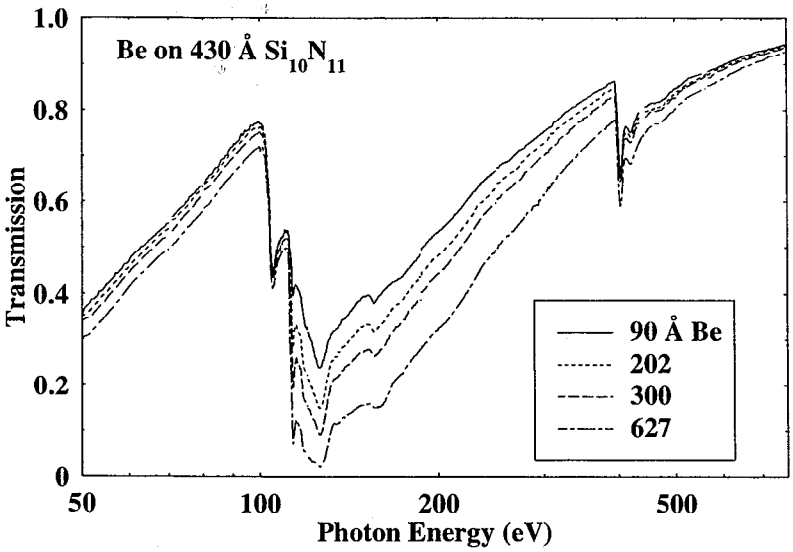

Figure 1. Transmission results are shown, obtained from beryllium films of 4 different thicknesses, each deposited on 430 Å of silicon nitride (see item *iii)* in Sec. 3). Features due to the silicon $L_{2,3}$ edge (99.8 eV), beryllium K edge (111.7 eV) and nitrogen K edge (410 eV) are clearly visible in this plot. The absorption coefficient μ of beryllium was obtained from these measurements by means of the technique outlined in eq. (5) and Fig. 2 below. This method is best suited for curves well-separated in transmission at each photon energy point, therefore only the portion from 111 to 250 eV of the illustrated set of curves was used for the determination of μ.

3. EXPERIMENT

The experimental data presented in this work were collected from 3 sets of transmission measurements in 3 energy regions within the range from 40 to 250 eV. A different set of free-standing beryllium foils was used in each case, as described below:

i) In 40-50 eV, transmission data were obtained from three foils with thicknesses of 0.5, 1 and 2 μm. The samples were fabricated at Lawrence Livermore National Laboratory (LLNL) by DC-magnetron sputtering, and were measured with a laser-plasma-based EUV source,[6] located at the Center for X-ray Optics, Lawrence Berkeley National Laboratory (LBNL).

ii) In 50-111 eV, two beryllium foils (0.7 and 1 μm), deposited by evaporation, were purchased from Lebow Company, Goleta, CA. Transmission measurements on these samples were performed at the Advanced Light Source (ALS) beamline 6.3.2,[7] at LBNL.

iii) For measurements in the region 111-250 eV, 4 beryllium foils supported by silicon nitride membranes were fabricated at LLNL. The membranes were designed to have an atomic composition of silicon:nitrogen = 10:11, a density of about 3 g/cm^3, a thickness of 430 Å and were deposited on 6-inch silicon wafers using the low-pressure chemical-vapor-deposition method. A 5×5 grid of 1.25×1.25 mm^2 windows was patterned with photoresist at the center of the silicon wafer and was etched using parallel-plate reactive-ion etching. Beryllium films of 4 different thicknesses (90, 202, 300 and 627 Å) were DC-magnetron sputtered on top of the silicon nitride, and the transmission of the beryllium-coated windows was measured at beamline 6.3.2. at the ALS. The transmission versus photon energy curves obtained from these samples are shown in Fig. 1.

The technique used to extract the absorption coefficient μ (cm^2/g) from the aforementioned experimental data is outlined in Fig. 2, and has also been described in previous papers.[8,9] The expression

$$T = T_0 \exp(-\mu\rho x) \tag{5}$$

is used for the transmission T, where x (cm) is the beryllium thickness in the foil and T_0 is the transmission from other material layers present in the foil. ρ=1.845 g/cm^3 was used for all samples mentioned in *i), ii)* and *iii)*. Eq. (5)

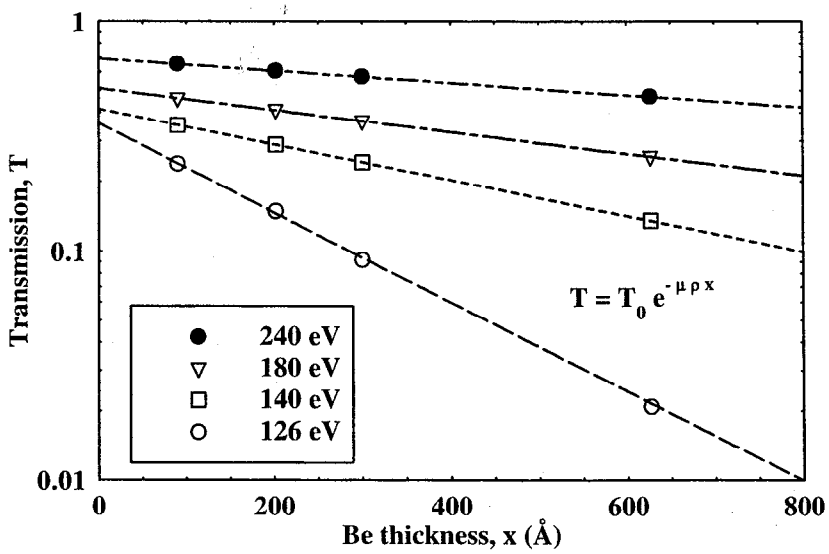

Figure 2. An example of the procedure for the determination of μ (cm^2/g) of beryllium is shown for a few photon energies. At each energy, μ is inferred from the slope of the transmission versus beryllium thickness curve (on a logarithmic scale). The experimental data points are obtained from the results shown in Fig. 1. The same technique has been applied in order to obtain μ in the energy range below the beryllium K edge, using transmission data from thicker foils described in Sec. 3, *i), ii).*

yields μ and T_0 at each photon energy point, assuming that (ρx) is accurately known and that each of the foils used in a measurement produces identical T_0. Thus, in order to obtain meaningful results from this method, it is important to have independent measurements of the density and/or thickness of the samples, and to establish that layers other than beryllium have similar thickness and composition among samples in the same set.

For the samples mentioned in *i), ii),* the mass per unit area (ρx) of beryllium was verified to within 5% using the α-particles method.[8] Native oxide, forming on a beryllium surface when it is exposed to air, was also expected to be present on the foils. Since all samples in each set were fabricated and handled under identical conditions, it was reasonably assumed that they would exhibit similar oxide thicknesses. Fitting of the T_0 curve for the 0.7 and 1 μm samples measured in *ii)* revealed a total of 300 Å of oxide present on both sides of the surface. This somewhat excessive oxide thickness was justified by the sample preparation process, which included rinsing in de-ionized water. In case *iii),* reflectivity vs. incidence angle measurements were performed in an area outside the etched center of the coated silicon wafers, for each of the samples in the set. The presence of layers (beryllium oxide, beryllium, silicon nitride) on the silicon wafer produced interference fringes in the reflectivity curve. By fitting the fringe widths, the thickness and density of the material layers in each foil was verified with an accuracy of 2%. From these fits, the silicon nitride membrane density was invariably estimated to be 2.9 g/cm^3; its thickness varied from 420 to 450 Å among the 4 samples. Furthermore, a beryllium oxide thickness of 35-40 Å was determined to be present on each sample.

4. RESULTS AND DISCUSSION

Fig. 3 (inset) shows the experimental values obtained in this work for the absorption coefficient μ (cm^2/g) of beryllium in the region 40-250 eV. Energy was scanned in 0.1, 0.25 and 0.5 eV steps. The error bars are due to possible slight variations in the residual film thickness responsible for T_0 and/or uncertainties in the beryllium thickness determination, as explained in Sec. 3. It was found that, in the energy region below the K edge, where the foils described in *i), ii)* were measured, such inaccuracies would affect the determination of μ to within 12%, while in the energy range above the K edge, μ obtained from the samples in *iii)* would be accurate to within 20%. Transmission measurements at both instruments mentioned in Sec. 3 were reproducible to better than 0.5%, with the exception

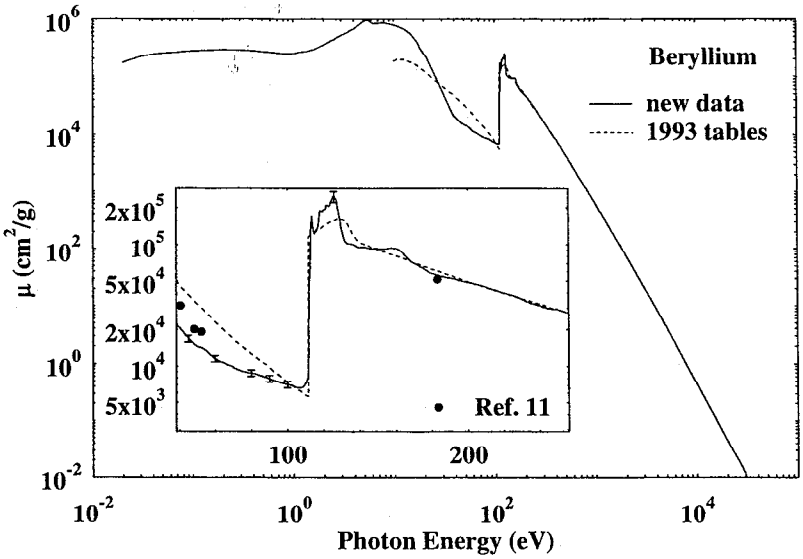

Figure 3. A new compilation of data for the absorption coefficient of beryllium is shown, including the experimental results in 40-250 eV presented in this work. Data from Refs. 5,10 have also been used in order to obtain a spectrum extending from 0.02 to 30,000 eV. The tabulated values[5] for μ in the range 10-30,000 eV are also shown for comparison. In the inset, the region around the K edge where transmission measurements were performed, is presented in detail. A few sample error bars are illustrating the magnitude of uncertainty in the experimental results, in the regions below and above the K edge. The data points (•) in Ref. 11 were obtained from measurements on 2500 Å-thick beryllium foils deposited on Par N membranes of various thicknesses. The authors of Ref. 11 acknowledged that μ (around 40 eV) may be overestimated by 25% due to the presence of oxide.

of the lowest energies and the regions of less than 10% transmission, where the reproducibility was around 1%. Higher harmonic and stray light suppression is achieved to better than 99% at the ALS beamline 6.3.2. and to better than 95% at the laser-plasma-based EUV source. Thus, the transmission measurement process did not make any significant contribution to the error budget. The most remarkable feature of these experimental results is their wide disagreement with the photoabsorption calculations in the 1993 atomic tables,[5] in the region below the K edge (40-111 eV). At 40 eV, the experimental absorption coefficient is more than a factor of 2 lower than the theoretical value predicted in Ref. 5. It is possible that, for a light material such as beryllium ($Z = 4$), the region below the K edge (corresponding to electrons of the outer shell) does not exactly obey the atomic-like behavior assumed in the model used in Ref. 5. Previously published experimental data points[11] are also shown in the inset of Fig 3, for comparison. In the region just above the K edge, fine structure is present. Such resonances in the density of states of beryllium have been attributed to atomic as well as metallic processes.[12,13] The present results are in excellent agreement with the experimental spectra presented in Ref. 12, obtained from photoabsorption measurements on evaporated beryllium films deposited on carbon substrates. Recently, an advanced theoretical model for the optical absorption of solids has been developed.[14,15] This treatment is relying on a first-principles approach, allowing for the incorporation of many-body corrections and electon-hole interactions. The computed spectra for the absorption coefficient are in very good agreement with the present measurements, as is shown in Fig. 4.

The experimental results for μ in the energy range 40-250 eV were combined with data published in Ref. 10 in the region 0.02-22 eV, and with the tabulated values[5] for energies above 250 eV. This composite set of data for the absorption coefficient in the region 0.02-30,000 eV is shown in Fig. 3, and was used for the determination of the atomic scattering factors f_1, f_2, by means of the method described in Sec. 2. The results for f_1 and f_2 are shown in Fig. 5, superimposed to the values in the 1993 atomic tables.[5] The updated values for the atomic scattering factors are used for the calculation of the normal incidence reflectivity of Mo/Be multilayers in the energy region of interest for EUV lithography applications, as shown in Fig. 6. The Bragg peak is displayed in detail at an energy point just below the beryllium K edge, where the reflectivity of these optics reaches its maximum value. Compared

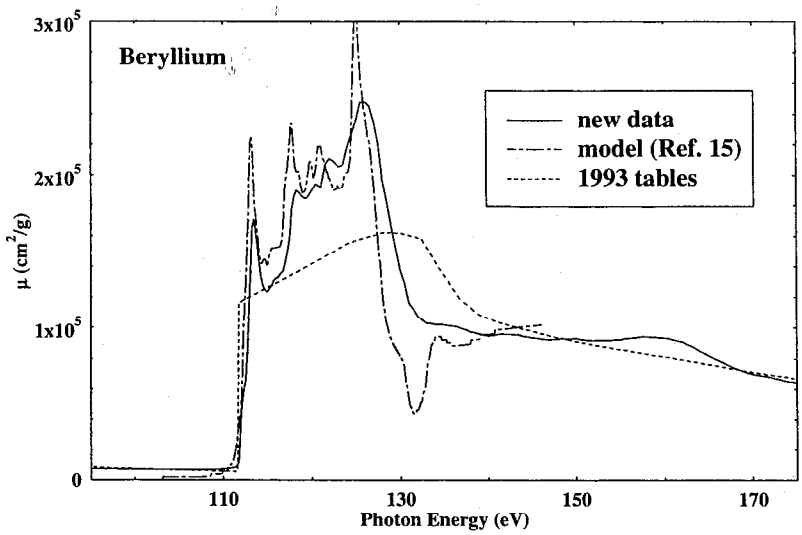

Figure 4. Fine structure in the energy region above the K edge of beryllium is plotted according to *(a)* the experimental results presented in this paper (solid line) and *(b)* calculations (dash-dot) based on a theoretical photoabsorption model,[14,15] taking into account many-body and electron-hole effects. Regarding the energy position of the peaks, there is good agreement between *(a)* and *(b)*. Differences in the peak heights could be attributed to adjustable parameters in the model. The sharp trough predicted by the theory at 131.6 eV was not reproduced in the measurements. Such a feature is related to assumptions about the electron lifetime, which is difficult to treat rigorously in the region extending a few tens eV above the K edge.[15] The simplified calculations in the 1993 atomic tables[5] are also shown (dash), which fail to capture the K-edge structure.

to the atomic scattering factor values in the 1993 tables, the updated results for f_1, f_2 yield similar results for the reflectivity at energies very close to the K edge. However, at lower energies (longer wavelenghts), the two sets of atomic scattering factors yield different results for the modeled reflectivity of Mo/Be optics.

5. CONCLUSIONS

Absolute photoabsorption results for beryllium are presented in the photon energy region from 40 to 250 eV. These experimental values are implemented in the calculation of the beryllium atomic scattering factors. The experimental absorption data in the region below the K edge appear to be much lower than the values predicted in the simplified calculations published in the 1993 atomic tables.[5] The effect of these results in the modeling of the reflectivity of Mo/Be multilayer optics is also demonstrated. A series of resonances is found in the experimental spectra above the K edge, which agrees well with previous measurements[12] and a recent theoretical computation.[14,15]

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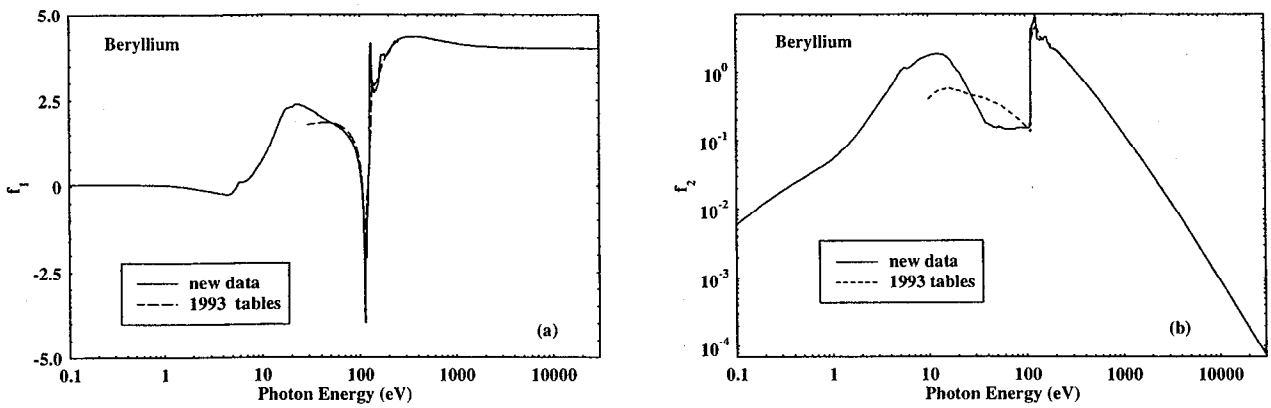

Figure 5. The *(a)* real and *(b)* imaginary parts of the atomic scattering factor $f = f_1 - if_2$ of beryllium are shown in the energy range 0.1-30,000 eV. f_2 is plotted on a logarithmic scale. The results are compared to the tabulated data[5] (dashed line).

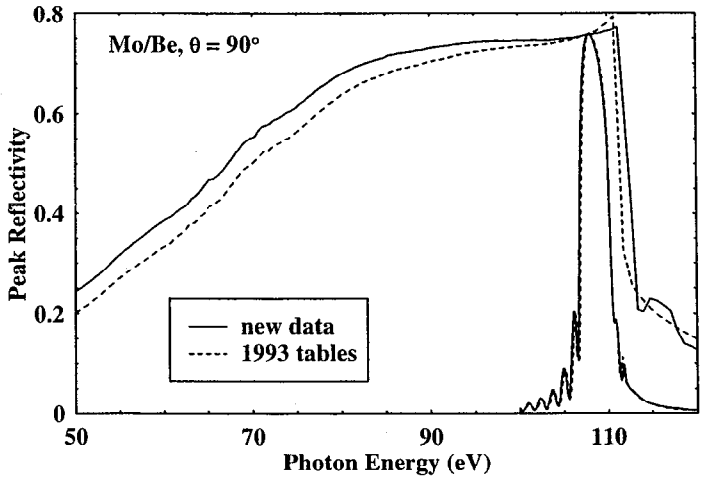

Figure 6. The peak reflectivity of Mo/Be multilayer optics is calculated versus photon energy, at normal angle of incidence. An infinite number of bilayers is assumed in the model, and the bilayer thickness is optimized at each energy point. The Bragg peak corresponding to a mirror with 70 bilayers and an individual bilayer thickness of 58 Å is shown in its entirety near the K edge. Modeling is performed using the atomic scattering factors of beryllium from the present work (solid line), as well as the tabulated values[5] (dashed line).

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